

Short communication

Effect of carbon coating on elevated temperature performance of graphite as lithium-ion battery anode material

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Abstract

The effect of carbon-coating on the elevated temperature performance of Li|graphite half-cells is investigated for 1 M LiPF₆ in PC|EC|DEC (3:2:5) and 1 M LiBF₄ in EC|DMC (2:1) electrolytes (PC = propylene carbonate; EC = ethylene carbonate; DEC = diethyl carbonate; DMC = dimethyl carbonate). Carbon-coated graphite is prepared by mixing synthetic graphite particles with polyvinylchloride powders, followed by heating to 1000 °C under a flow of argon gas. For LiPF₆-based cells, when pre-cycled cells are stored at 80 °C and then cycled at 30 °C, the loss of charge after storage at elevated temperature is much less with carbon-coated graphite than with untreated graphite electrode. When cycled at 80 °C without pre-cycling, the carbon-coated graphite electrode shows stable cycling behaviour, but untreated graphite results in premature cell failure. It appears that the carbon-coating preserves the graphite electrode even after storage at 60 °C in LiBF₄-based electrolyte. From cycling and storage tests, it is concluded that surface modification through carbon-coating is very effective for the improvement of electrochemical performance and thermal stability of graphite electrodes at elevated temperatures.

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1. Introduction

Graphite is employed as an anode material in many commercially available lithium-ion batteries. During the first charge–discharge cycle of such a battery, a passivating solid electrolyte interface (SEI) layer is formed on the external surface of the graphite. Formation of the SEI layer inevitably involves irreversible capacity loss, but also protects the graphite from co-intercalation of solvent molecules between the graphene layers [1–4].

The above mentioned irreversible reactions can also cause gas evolution, which may result in safety problems [1]. The irreversible capacity associated with the graphite electrode varies considerably with the choice of electrolyte. Ethylene carbonate (EC)—based electrolyte mixtures such as EC|DEC (diethyl carbonate) are used widely in lithium-ion batteries, whereas the use of PC (propylene carbonate)—based electrolyte has been avoided because PC continues to decompose during the intercalation process.

This decomposition results in exfoliation of the graphene layer which in turn, gives rise to a large irreversible capacity during cycling [3,5]. Nevertheless, PC is a very attractive solvent in view of providing a high conductivity electrolyte even at low temperature, which is mainly due to its low melting point. One common approach to suppress the irreversible solvated intercalation of lithium into graphite is to modify existing graphites by coating carbon on to the graphite surface. The resultant carbon-coated graphites showed great improvement in the electrochemical performance as an anode material in PC-based electrolyte [6–9]. These studies have, however, been carried out at room temperature. Moreover little work has been performed on the thermal stability of the carbon-coated graphite electrodes.

For wide applicability, lithium-ion cells should be utilized safely at elevated temperatures. Safety is mainly related to the thermal reactivity of the cell components. It has been shown that the thermal stability of graphite electrodes is critically dependent on the choice of the electrolyte solution, particularly the lithium salt used in the electrolyte [10–16].

This study examines whether modification of graphite by carbon-coating can be effective in assuring good electrochemical performance as an anode at elevated temperatures.

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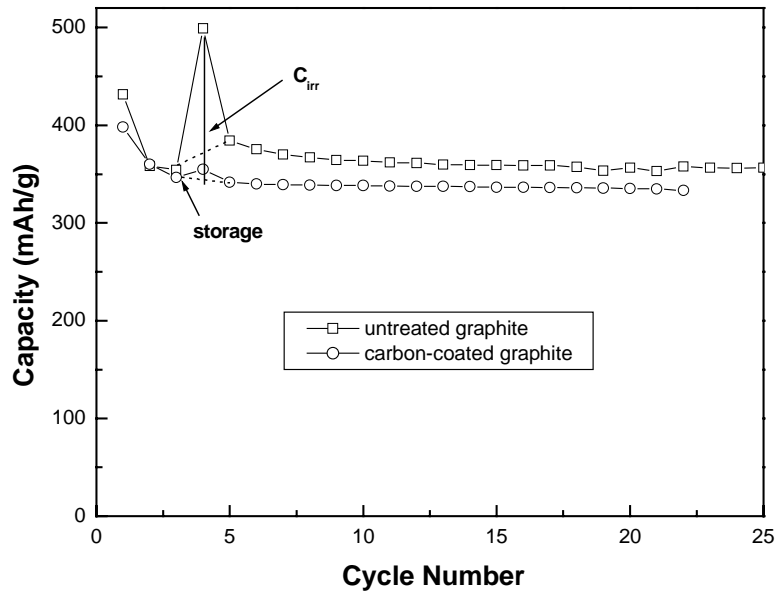


Fig. 1. Total reduction charge vs. cycle number for half cells with untreated graphite or carbon-coated graphite electrodes. The cells were pre-cycled for three cycles at 30 °C prior to storage at 80 °C for 7 days in a de-intercalated state, and then cycled at 30 °C. The electrolyte was 1 M LiPF_6 in PC|EC|DEC .

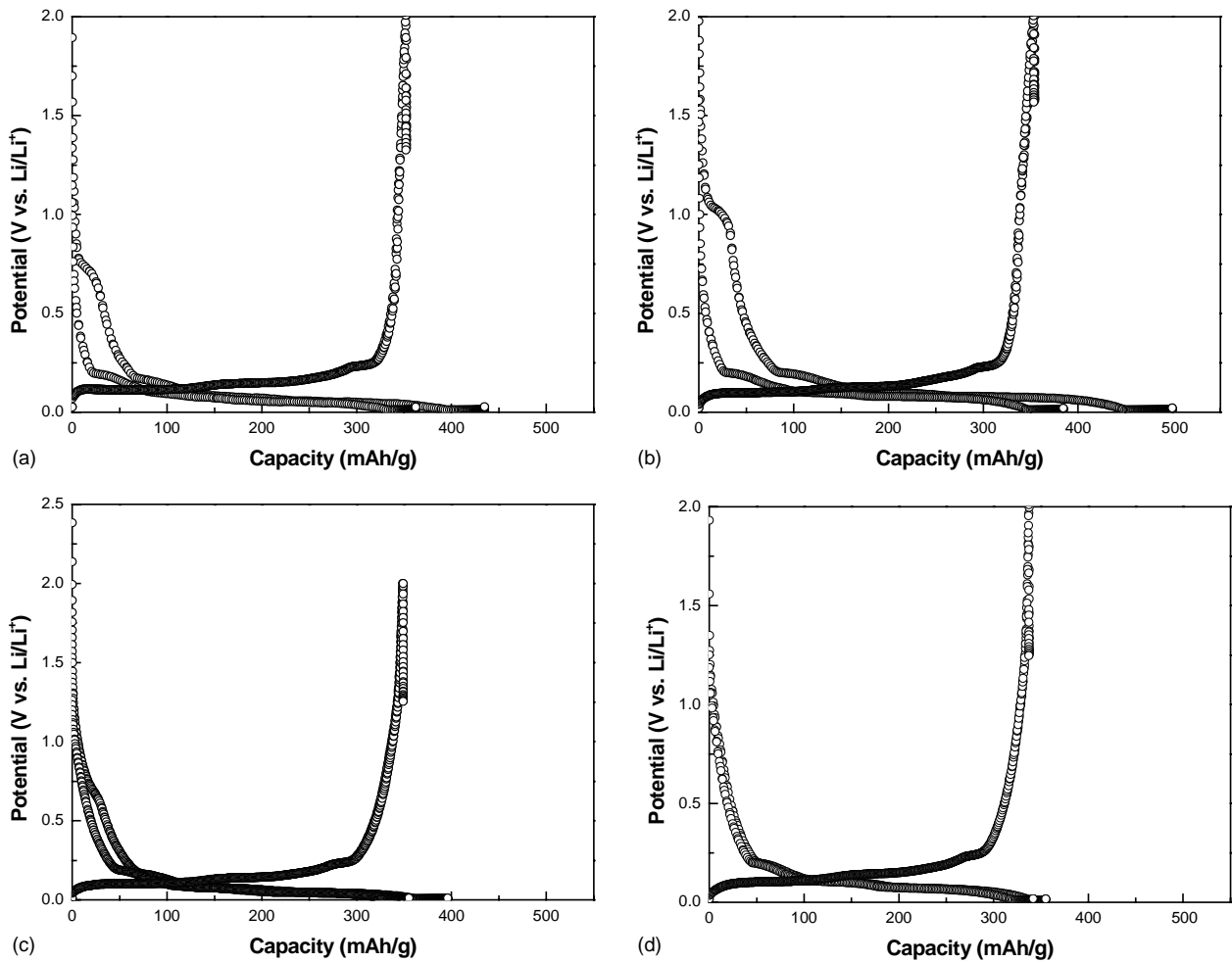


Fig. 2. Voltage vs. capacity for first two cycles at 30 °C (a), (c) before and (b), (d) after storage at 80 °C for 7 days, as illustrated in Fig. 1: (a) and (b) untreated graphite; (c) and (d) carbon-coated graphite.

Accordingly, an investigation is made of the behaviour of carbon-coated graphite electrodes at elevated temperatures during cycling and storage in half-cells, assembled with LiPF_6 PC|EC|DEC and LiBF_4 EC|DMC electrolyte solutions (DMC = dimethyl carbonate).

2. Experimental

Synthetic graphite (SFG-6, Timcal) was used in this study carbon-coated graphite was prepared by heating a mechanical mixture of graphite and 170 wt.% PVC powder at 1000°C for 1 h under an argon flow [9].

A coin cell with a graphite anode and a counter electrode of lithium metal foil was used in all experiments. The graphite electrodes were prepared by mixing 90 wt.% graphite with 10 wt.% PVDF (polyvinylidene fluoride) binder dissolved in *n*-methylpyrrolidinone (NMP). The slurry was spread on to a copper grid. The electrodes were then dried for 12 h at 120°C in a vacuum oven. The electrolyte solutions were: 1 M LiPF_6 in PC|EC|DEC (3:2:5; v/o) and 1 M LiBF_4 in EC|DMC (2:1; v/o) and were provided by Cheil Industries Inc., Korea. All cells were fabricated in an argon-filled glove box.

The cells were cycled between 0.01 and 2.0 V with a relaxation period of 10 min at the end of each discharge–charge, at a constant current of 0.3 mA cm^{-2} . The electrochemical measurements to examine the thermal stability during storage at elevated temperatures were made by first pre-cycling equivalent cells galvanostatically at room temperature for three cycles. The cycling was interrupted when the cells were either at the low cut-off voltage (0.01 V), with the

graphite in its fully-intercalated state, or at the high cut-off voltage (2.0 V), in the de-intercalated state. The LiPF_6 - and LiBF_4 -containing cells were then stored at 80 and 60°C for 7 days under open-circuit conditions, respectively. After storage, the cells were cycled at 30°C , starting with a intercalation reaction.

3. Results and discussion

It has been well known that the SEI film formed during initial cycles at room temperature provides a passivation layer for the graphite grains and thus prevents other undesirable side-reactions. During storage at elevated temperatures, however, the SEI layers are degraded by temperature-induced reactions between the SEI and the electrolyte species, which may result in a decline in capacity and premature cell failure.

The total reduction charge as a function of cycle number is shown in Fig. 1 for Li|graphite half cells, which were pre-cycled for three cycles at 30°C prior to storage at 80°C for 7 days and then cycled at 30°C . The cells were stored in their de-intercalated states. The electrolyte was 1 M LiPF_6 in PC|EC|DEC. For the first discharge after storage (i.e., cycle 4), the additional reduction charge (marked as C_{irr}) indicates irreversible capacity loss, which is significantly smaller for a carbon-coated graphite than for an untreated one, although these latter cells cycled well without capacity loss after storage. This irreversible capacity is mainly attributed to additional reduction of the electrolyte as inferred from the discharge curves for cycle 4 shown in Fig. 2, in which a reduction plateau around 1.0 V; related to the new SEI

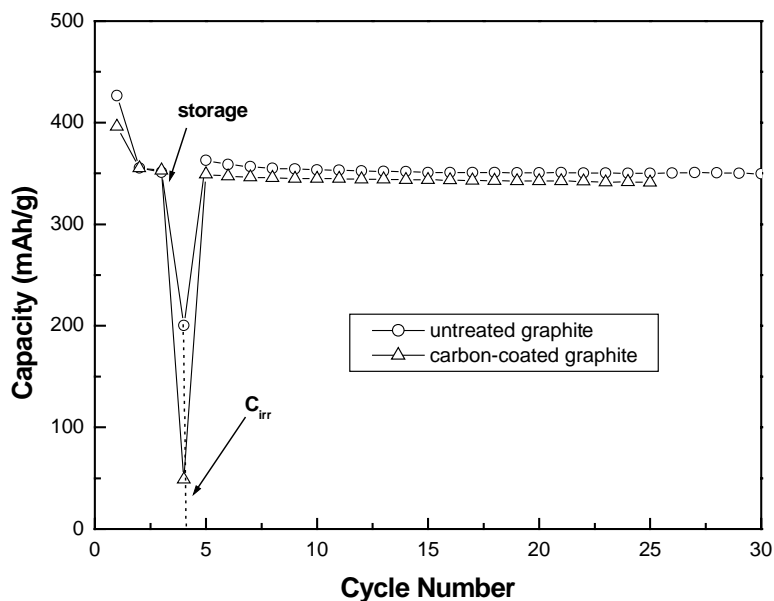


Fig. 3. Total reduction charge vs. cycle number for half cells with untreated graphite or carbon-coated graphite electrodes. The cells were pre-cycled for three cycles at 30°C prior to storage at 80°C for 7 days in intercalated state, followed by continued cycling at 30°C . The electrolyte was 1 M LiPF_6 in PC|EC|DEC.

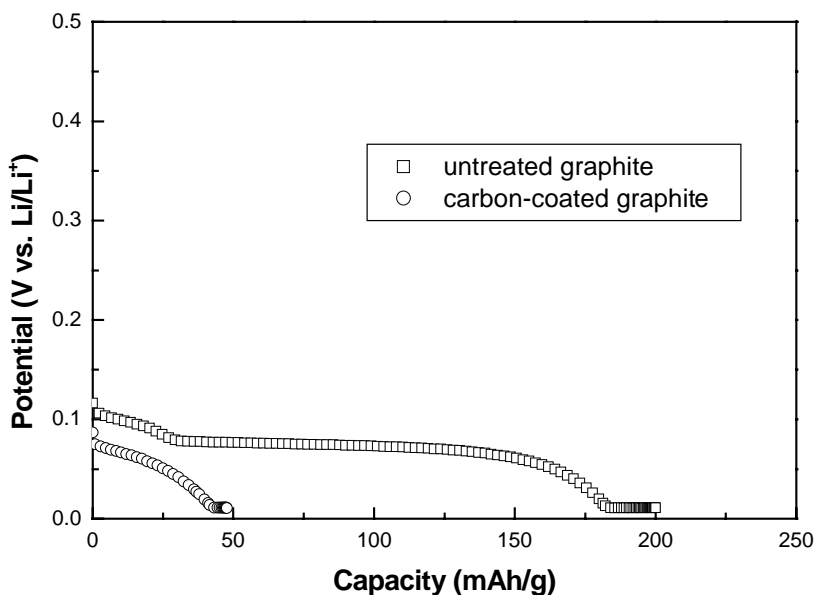


Fig. 4. Voltage profiles of untreated and carbon-coated graphite electrodes for first lithium intercalation after storage, as illustrated in Fig. 3.

formation, is observed for the untreated graphite electrode while for the carbon-coated sample little additional reduction reaction occurs. As a result of the rearrangement of the original SEI layer during storage, a porous SEI structure is created, which leads to penetration of electrolyte species to the graphite surface and thus the formation of a new SEI film during the first cycle after storage [14]. Given that the SEI layer is formed at the edge sites on graphite and that these are the dominant active sites for electrolyte decomposition [5], it is believed that carbon coated on the graphite suppresses effectively the additional electrolyte decomposition to form a new SEI layer by covering the active edge sites.

A similar plot of capacity data for a cell stored in the intercalated state is presented in Fig. 3. The capacity (C_{irr}) on

the first cycle after storage is associated with the depletion of lithium in the graphite, dissolution of the SEI layer or any other side reaction that leads to a loss of capacity [14]. This irreversible capacity appears to be much larger for an untreated graphite than for a carbon-coated electrode. It is also noted that, in the case of carbon-coated graphite electrode, the amount of the irreversible capacity on the fourth cycle is comparable with that on the first cycle. The large difference in C_{irr} between the two cells can be explained by a quite different potential curve on the fourth cycle, as shown in Fig. 4. The large irreversible capacity for the untreated graphite electrode is attributed mainly to additional electrolyte decomposition and to the formation of a new SEI layer since a reduction plateau near 0.8 V is caused by these

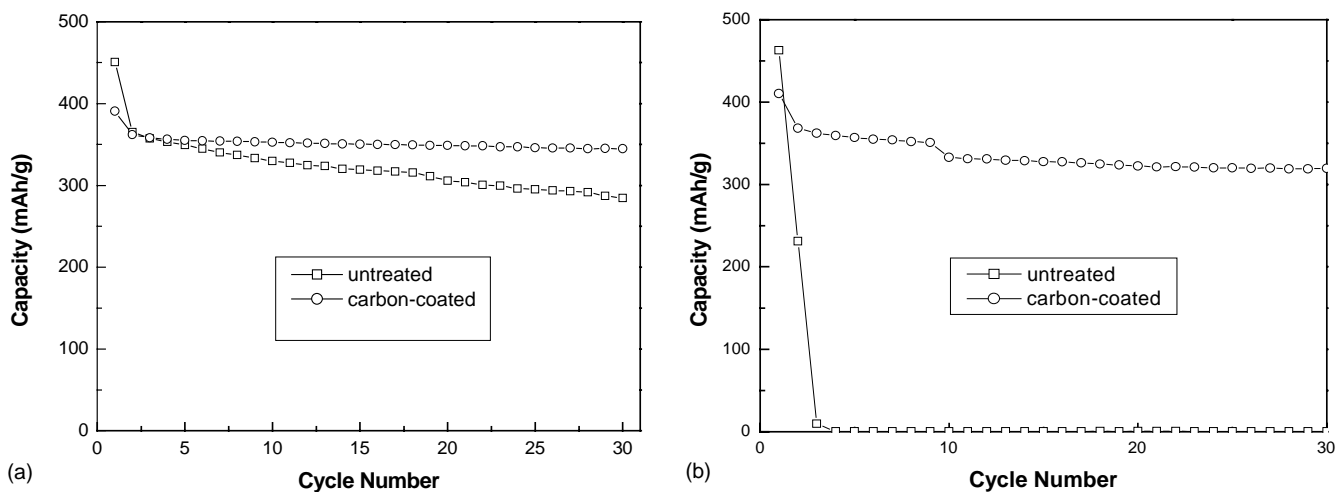


Fig. 5. Capacity vs. cycle number for untreated and carbon-coated electrodes at: (a) 30 °C and (b) 80 °C. Note that cycling at 80 °C was performed without pre-cycling at 30 °C. The electrolyte was 1 M LiPF₆ PC|EC|DEC.

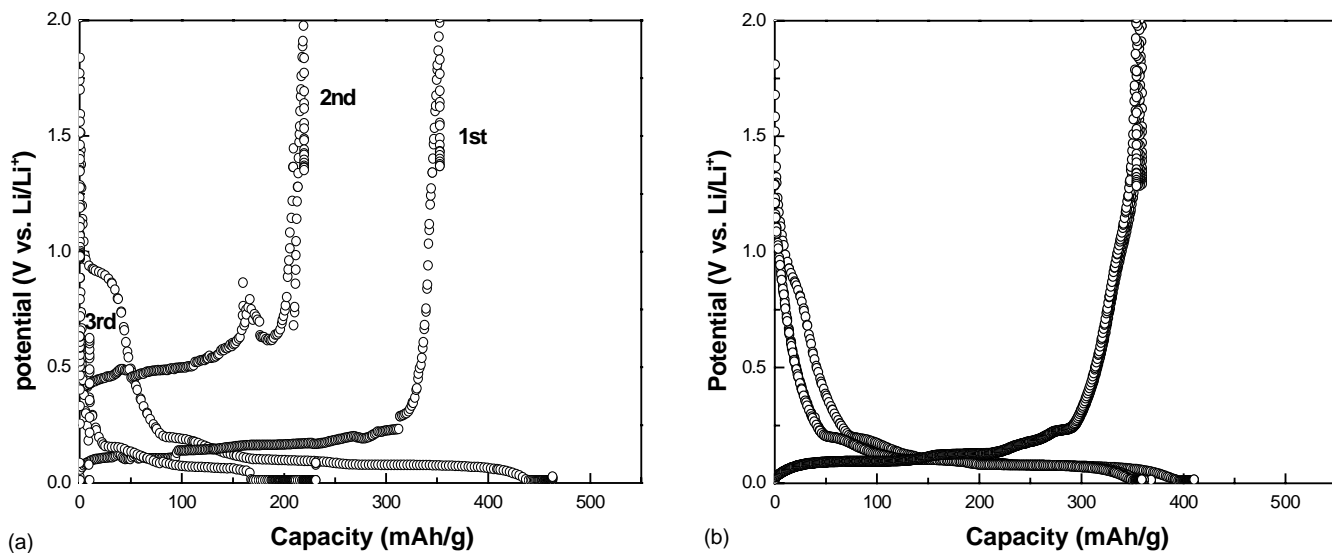


Fig. 6. Charge–discharge curves for the first two cycles at 80 °C, as illustrated in Fig. 5(b): untreated graphite electrode and carbon-coated graphite electrode.

side reactions [14]. The large increase of C_{irr} on the fourth cycle compared with the first cycle indicates that many active sites are created during storage at an elevated temperature of 80 °C and result in a large irreversible capacity as illustrated by a long plateau-like profile around 0.8 V. On the other hand, the potential curve for the cell with the carbon-coated electrode seems to be related to re-intercalation of lithium into graphite rather than to any side reactions that form a new SEI layer.

These results indicate that, as the result of storage at 80 °C, graphite surfaces are exposed to electrolyte and some additional sites become active for SEI film formation on

subsequent cycling at room temperature. By contrast, SEI film formation is effectively suppressed by carbon-coating treatment. It should be noted, however, that no destructive reactions such as graphite exfoliation occur because no intercalation capacity is lost on continued cycling after storage of both cells.

Capacity as a function of cycle number for carbon-coated and untreated electrodes when cycled at 30 and 80 °C without pre-cycling at 30 °C is shown in Fig. 5. A dramatic effect of temperature on cycling behaviour is observed for the untreated electrode while the carbon-coated graphite appears to be quite stable even at 80 °C. At the higher

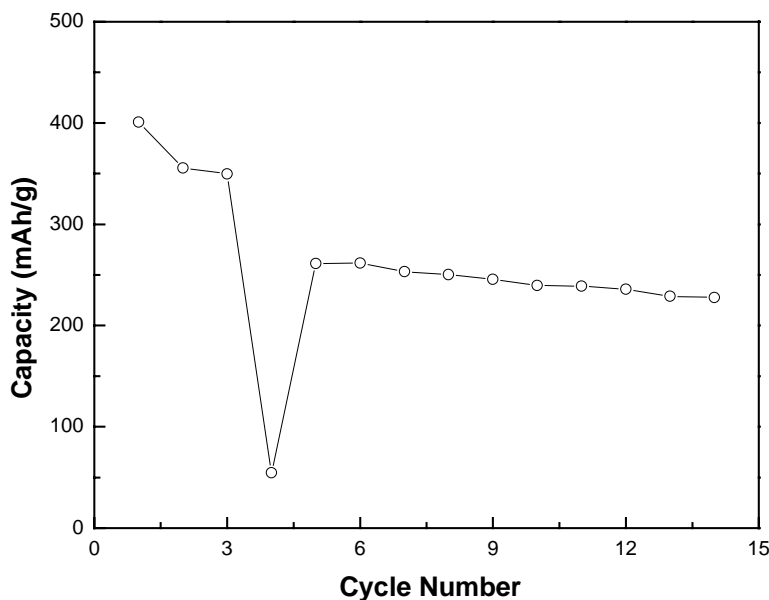


Fig. 7. Total reduction charge vs. cycle number for half cell with carbon-coated graphite electrode. The cell was pre-cycled for three cycles at 30 °C prior to storage at 60 °C for 7 days. The electrolyte was 1 M LiBF₄ EC|DMC.

temperature the cell with untreated graphite fails after three cycles. This dissimilar behaviour is illustrated by the first and second charge–discharge curves for both samples (Fig. 6). In the case of untreated graphite, the SEI film formed during the first cycle at the elevated temperature of 80 °C is not protective and results in degradation of the electrode. This is probably due to the percolation of electrolyte solution into the graphite. Judging from the above, it can be concluded that the surface modification by carbon-coating renders graphites stable for storage/cycling in LiPF₆ PC|EC|DEC electrolyte, not only at room temperature but also at elevated temperature.

It has been reported [11,14] that storage of graphite electrodes in LiBF₄ EC|DMC at 60 °C deteriorates the cycling performance significantly. In this connection, similar tests have been performed on a carbon-coated graphite|Li half cell to investigate the effect of carbon-coating on the thermal stability of the graphite electrode. Carbon-coating allows reasonable cycling performance at room temperature, even after storage in LiBF₄-based electrolyte at elevated temperature, as shown in Fig. 7. There is little capacity loss after storage at 60 °C. It is considered that the thermal stability of graphite at elevated temperatures would be further improved if the carbon-coating over the graphite particles becomes more uniform and dense, and thereby protects the graphite from electrolyte attack more effectively.

4. Conclusions

Based on the results of cycling and storage tests of Li|graphite cells at elevated temperatures using 1 M LiPF₆ PC|EC|DEC and 1 M LiBF₄ EC|DMC electrolytes, it is concluded that surface modification by coating with PVC–carbon improves significantly the electrochemical performance and thermal stability of graphite electrodes at elevated temperatures. This is because a PVC–carbon

coating layer with a turbostratic structure protects graphite grains from electrolyte attack.

Acknowledgements

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